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Title of the Invention: Manufacturing method of semiconductor thin film

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SPECIFICATION

1. Title of the Invention

Manufacturing method of semiconductor thin film

2. Scope of Claims for Patent

1. A method of manufacturing a semiconductor thin film comprising the steps of:

forming a silicon thin film layer on a glass substrate;

coating said silicon thin film layer with a paste, which is formed by dispersing tin fine particles into organic solvent;

cooling down slowly after heating the glass substrate at 232°C.

2. The method of claim 1 further comprising the step of coating the silicon thin film layer in a matrix form with a paste, which is formed by dispersing tin fine particles into organic solvent.

3. Detailed Description of the Invention

#### [FIELD OF THE INDUSTRIAL APPLICATION]

The present invention relates to a method of manufacturing a semiconductor thin film, and in more detail, to a method of forming a polysilicon thin film on a glass substrate having large area.

#### [PRIOR ART AND PROBLEMS]

As a driving method of display devices such as a liquid crystal display, there are several kinds of method, and in particular, a matrix system has been noted in recent years since it is possible to realize high quality image and large display capacitance.

According to the system, a semiconductor thin film is formed on a transparent glass substrate. In the semiconductor thin film, a substrate having switching elements such as a thin film diode or a thin film transistor arranged in a matrix form. By using the switching elements, a liquid crystal cell so as to form each pixel is directly driven.

Fig. 9 shows an equivalent circuit of a matrix driving type liquid crystal display in which a thin film transistor 10 is used as switching elements. In Fig. 9, reference numeral 11 is a scanning line, 12 is a signal line, and 13 is a liquid crystal cell. Then, the thin film transistor 10 as switching elements and the liquid crystal cell 13, which are connected each other, are arranged in a portion divided by each scanning line 11 and signal line 12, thereby forming one pixel of a liquid crystal display.

Such an equivalent circuit of a liquid crystal display is formed in a semiconductor thin film, which is formed on a transparent glass substrate. As a material of the semiconductor thin film, a hydrogenated

amorphous silicon thin film, which is formed by a plasma CVD method, is mainly utilized. This is because that it is possible to form an amorphous silicon thin film having large area at low temperature of glass softening point or less by using the plasma CVD so as to make it a substrate of a liquid crystal display wherein the size of diagonal is about several inches, the scanning line 11 and the signal line 12 are several hundreds, respectively, and the number of all the pixels is about several hundred thousands.

By the way, in recent years, requirement of a display having large area is more and more increasing. It is necessary to form a thin film transistor 10 with high switching speed in a semiconductor thin film having large carrier mobility in order to manufacture a liquid crystal display having large area wherein the scanning line 11 and signal line 12 are one thousand or more, respectively, and the number of all the pixels is several millions or more.

However, the above mentioned hydrogenated amorphous silicon thin film has a small carrier mobility of  $1\text{cm}^2/\text{vs}$  at most, so that there is a limit of improvement in switching speed. Accordingly, it is proposed to use a polysilicon thin film having larger carrier mobility.

The polysilicon thin film can be formed by an LPCVD (Low Pressure Chemical Vapor Deposition) method or a laser annealing method.

In the LPCVD method, a polysilicon thin film is directly deposited on a heated glass substrate by using silane gas as a material. According to the LPCVD method, however, crystal grains of the polysilicon thin film cannot be sufficiently grown because it is impossible to raise the temperature of thin film formation higher than a glass softening point. The carrier mobility of a semiconductor thin film depends on the size of crystal grain diameter and the crystallinity thereof, so that there is a limit to the carrier mobility of the polysilicon thin film formed by the LPCVD method, which is about ten times as high as that of an amorphous thin film.

On the other hand, in the laser annealing method, a semiconductor thin film is formed on a glass substrate beforehand, followed by irradiating with laser light to melt-recrystallize, so that it is possible to sufficiently grow the crystal grain having good crystallinity. Because of this, the carrier mobility can be  $100\text{cm}^2/\text{vs}$  or more and device having enough switching speed for driving liquid crystal display, wherein the number of pixels reaches to several millions, can be formed. In the laser annealing method, however, it takes a lot of time to treat a substrate having several millions of pixels even if processing time per pixel is one second because laser light is irradiated corresponding to each pixel. As a result, there arises a problem that the laser annealing method is not suitable for mass production.

In view of the foregoing problems, the present invention has been made. It is an object of the invention to provide a method of forming a polysilicon thin film having large crystal grain diameter and excellent crystallinity on a glass substrate having large area in a matrix form in order to realize high throughput.

#### [MEANS TO SOLVE THE PROBLEMS]

In the manufacturing method of a semiconductor thin film according to claim 1 in the present invention, means to solve the problems comprises the steps of; forming a silicon thin film layer on a glass substrate; coating the silicon thin film with a paste, which is formed by dispersing tin fine particles into an organic solvent; and slowly cooling down the glass substrate after heating up to a temperature of  $232^\circ\text{C}$  or higher. Further, in the manufacturing method according to claim 2 in the present invention, means to solve the problems comprises that paste, which is formed by dispersing tin fine particles into an organic solvent, is coated on a silicon thin film layer in a matrix form.

#### [OPERATION]

After the silicon thin film is coated with a paste, which is formed by dispersing tin into an organic solvent, a melting layer of a binary

alloy between silicon and tin can be formed in the coated portion by heating. Subsequently, when it slowly cooled down, it is possible to make silicon crystal grow from the surface of the melting layer to the side of the glass substrate. This is because cooling of the melting layer side, which has larger thermal conductivity than the glass substrate, is firstly conducted.

This invention will be explained in more detail below.

The manufacturing method of a semiconductor thin film according to the invention comprises the steps of; (1) forming a silicon thin film on a glass substrate; (2) coating the silicon thin film with a paste; (3) heating the substrate which is coated with the paste; and (4) cooling the heated substrate.

The present invention will be explained below in order of process.

Fig. 1 and Fig. 5 show a method of manufacturing according to the present invention in order of process.

#### 1. Process of forming a substrate

Initially, as shown in Fig. 1, a glass substrate 1 having smooth surface is prepared. The glass substrate 1 is washed by detergent and acid solution in order to clean the surface.

Then, as shows in Fig. 2, a silicon thin film layer 2 is formed at a thickness of 1 to 2  $\mu\text{m}$  on the glass substrate 1. The silicon thin film layer 2 may be either an amorphous silicon thin film or a polysilicon thin film. Such a silicon thin film layer 2 can be formed by known methods such as a plasma CVD or an LPCVD method.

#### 2. Coating process

Then, as shown in Fig. 3, a tin coated layer 3 is deposited on the silicon thin film layer 2 in a matrix form.

In order to form such a tin coated layer 3, it can be suitable method that a paste, which is formed by dispersing tin fine particles having a grain diameter of  $1\mu\text{m}$  or less into organic solvent such as polyvinyl alcohol, is applied by using several kinds of printing methods such as a relief-printing method, an intaglio-printing method, and a

screen process printing method. The printing method and the coating condition can be properly selected depending on a controllability of the thickness of paste, a pattern formation ability which corresponds to each matrix, a controllability of the position of coated region over a large area substrate, or the like. Also, the pattern and the pitch of the tin coated layer 3 are necessary to be decided in order that tin coated layers 3 and 3, which are adjacent to each other, may not be in contact with each other because the tin coated layer 3 is expanded in the case of melting.

According to the example shown in Fig. 3, it should be noted that the tin coated layer 3 is coated on the silicon thin film layer 2 in a matrix form, however the manufacturing method of the present invention is not limited to this example. In other words, the tin coated layer 3 may be formed on the entire surface of the silicon thin film layer 2.

### 3. Heating process

Then, a glass substrate 1 on which the tin coated layer 3 is heat-treated. This process is conducted to heat the silicon thin film 2 and the tin coated layer 3 to form a melting layer 4 of a binary alloy between silicon and tin. This process can be conducted after a cooling process 4 described below in series, for example, in an electric furnace which is kept in an inert atmosphere such as nitrogen.

In the case of using an electric furnace, an example of temperature condition between heating and cooling is shown in Fig. 6. The temperature increase is performed by at about  $+10^{\circ}\text{C}$  per minute slow enough to avoid thermal deformation of the glass substrate 1 to a temperature higher than temperature T where the binary alloy between silicon and tin melts. This temperature T can be determined with reference to the Fig. 7.

Fig. 7 shows a schematic view of a binary alloy between silicon (Si) and tin (Sn). As is apparent from the Fig. 7, in a binary alloy melting liquid which is rich in tin, solid phase of silicon, that is, crystal is deposited at a temperature of  $230^{\circ}\text{C}$ , so that the temperature is



increased from minimum of 232°C to maximum less than softening point of glass in this heating process.

When the glass substrate 1 is kept at the temperature of T or higher for a couple of minutes, a silicon thin film 2 and a tin coated layer 3 which is formed on the silicon thin film 2 are melted to form a melting layer 4 in a matrix form as shown in Fig. 4.

It should be noted the melting layer 4 is formed by melting not only a portion of the silicon thin film 2 just below the tin coated layer 3 but also a peripheral portion of the silicon thin film 2 around the tin coated layer 3. Accordingly, the area of the melting layer 4 is larger than that of tin coated layer 3.

#### 4. Cooling process

Then, the glass substrate 1 on which the melting layer 4 is formed is slowly cooled down. The temperature is also slowly decreased by about -10 °C per minute as the same way that the temperature is increased. Since the thermal conductivity of the alloy between silicon and tin is larger than that of glass, temperature distribution occurs from the surface of the melting layer 4 toward the side of the glass substrate 1. Firstly, crystal of silicon is segregated from the surface of the melting layer 4. Then, the crystal of silicon is grown toward the side of the glass substrate 1 while cooling down, and hence a polysilicon thin film 5 is formed in the silicon thin film 2 in a matrix form as shown in Fig. 5.

The polysilicon thin film 5 formed in this way is grown using the crystal, segregated on the surface of the melting layer 4, as a nucleus, so that it has large crystal grain diameter of about 10μm and also has excellent crystallinity. As a result, the number of grain boundaries in each matrix is around several, so that it is possible to obtain a polysilicon thin film having the same carrier mobility with the polysilicon thin film formed by laser annealing or larger carrier mobility than the polysilicon thin film formed by laser annealing.

According to the manufacturing method of the invention, the polysilicon thin film layer 5 is formed by depositing crystal of silicon

from the melting layer 4 of the alloy between silicon and tin. The crystal grain of silicon is grown from the side of the surface of the melting layer 4, so that tin is included in the surface of the polysilicon thin film layer 5 at several ppm or lower and the concentration of silicon is approximately 100%. Also, since tin is included in IVb group element as the same with silicon, it is inactive in view of electricity if it contaminated into silicon. When tin is contained in the portion of the side of the glass substrate 1 in the polysilicon thin film layer 5, the characteristic of semiconductor is not affected at all.

In addition, in an interface between the polysilicon thin film layer 5 and the glass substrate 1, the concentration of the tin is rapidly increased and on the contrary, the concentration of silicon is several % or lower. Therefore, for example, if a coplanar type thin film transistor is structured by using the polysilicon thin film layer 5, the surface of the polysilicon thin film layer 5 becomes a channel layer in which carrier moves so that the thin film transistor having an ideal structure can be obtained.

Further, according to the manufacturing method of the present invention, the tin coated layer 3 is formed on the silicon thin film layer 2 at one time by printing method. Therefore, in the case of using the glass substrate 1 having a large area, it is possible to shorten the time which is required to print per a glass substrate to several minutes and hence through put can be improved. Further, in the heating process and the cooling process, it is possible to treat a lot of the glass substrate 1 at the same time, thereby further improving in through put, that is, mass production.

In particular, according to the manufacturing method in claim 2 of the present invention, the tin coated layer 3 is formed on a fine region in a matrix form. Therefore, when the crystal of silicon is grown from the melting layer 4, it is possible to reduce the contact between each of crystal grains and to make crystal grain diameter grow in the size of approximately same with fine region in a matrix form. As a result, the

switching speed can be improved.

#### [EMBODIMENT]

A glass substrate in a rectangle form is prepared at a size of 600mm x 1000mm and the surface thereof is washed by detergent and acid solution in order to clean the surface. As shown in Fig. 2, on the one surface of the glass substrate is formed an amorphous silicon thin film at a thickness of 1 to 2 $\mu$ m by plasma CVD. It should be noted that silane gas is used as a material in the embodiment and the glass substrate is heated at 250°C. Then, said amorphous silicon thin film is coated with a paste, which is formed by dispersing tin fine particles having grain diameter of 1 $\mu$ m or less into polyvinyl alcohol, by an intaglio-printing method so as to form a tin coated layer in a matrix form at a thickness of 2 to 3 $\mu$ m as shown in Fig. 3. Each pattern of tin coated layers is in a square form having a size of 10 $\mu$ m x 10 $\mu$ m and the pitch between pattern and itself is 150 $\mu$ m in the horizontal direction and 450 $\mu$ m in the vertical direction. Also, the number of pattern is 6000 in the horizontal direction and 1000 in the vertical direction, which amounts to a total of 6 millions. It takes three minutes to print.

Next, a glass substrate in which the tin coated layer is formed is heated in an electric furnace, which is kept in a nitrogen atmosphere. It takes 30 minutes to heat up to 300°C, and the temperature of 300°C is kept for several minutes, followed by cooling down to the room temperature for 30 minutes. The amorphous silicon and tin are melted in this heating process and the area of a thin coated layer in a matrix form is increased to have the pattern of 20 $\mu$ m x 20 $\mu$ m, which is about four times as large as that in the coating process. According to this heating process, it is possible to conduct batch treatment of a lot of substrates, so that 50 glass substrates can be treated at one time, thereby improving in through put.

In order to examine crystal structure of the polysilicon thin film formed in this way, the surface of the polysilicon thin film layer is

etched with dilute hydrofluoric acid aqueous solution, followed by examining it with a differential interference microscope. Although the crystal grain of the polysilicon thin film formed by an LPCVD method is generally small of  $1\mu\text{m}$  or less, the crystal grain obtained by the manufacturing method of the present invention, is larger, that is  $10\mu\text{m}$  or more. In other words, in the pattern having the size of  $20\mu\text{m} \times 20\mu\text{m}$  in a matrix form, the number of grain boundaries is several or less. Also, the composition of the polysilicon thin film is examined with an ion micro analyzer (IMS) taken along the direction of thickness. As a result, silicon is included in the surface of the thin film at about 100% and tin is included at several ppm or less. Moreover, when dispersion in the number of grain boundaries between each of matrixes on the glass substrate, is examined, it is confirmed that the dispersion is twice or less in each of matrixes, which are separated by  $1000\text{mm}$  each other, so that an uniform thin film can be obtained even if it is large area substrate.

Then, the coplaner type electric field effect type thin film transistor as shown in Fig. 8 is formed on each polysilicon thin film which is formed in a matrix form in this way. This is formed by using usual manufacturing process of the thin film transistor. In Fig. 8, reference numeral 6 shows a source electrode, 7 shows a drain electrode, 8 shows a gate electrode, and 9 shows a gate insulating film, respectively. The channel length and channel width of the thin film transistor are  $5\mu\text{m}$  and  $10\mu\text{m}$ , respectively. The size of the thin film transistor is smaller than that of matrix pattern in the polysilicon thin film layer, which makes it possible that a thin film transistor is formed on each polysilicon thin film layer in the entire surface of the glass substrate.

When the carrier mobility of the polysilicon thin film layer is founded on the current and voltage characteristics of the thin film transistor which is formed in this way, the high value of about  $120\text{cm}^2/\text{vs}$  can be obtained. This value is as high as that of the thin film formed

by a laser annealing method. As a result, in the equivalent circuit as shown in Fig. 9, the liquid crystal display having large display capacitance wherein six million thin film transistors are comprised in total and high image quality, can be realized.

#### [THE EFFECT OF THE INVENTION]

As described above, according to the manufacturing method of the invention, crystal of the silicon is grown from melting liquid of the alloy between silicon and tin, so that the polysilicon thin film having large crystal grain diameter and good crystallinity. Therefore, it is possible to form a semiconductor thin film having a carrier mobility, which is enough for driving liquid crystal display having large area.

Also, according to the manufacturing method of this invention, it is possible to deal with substrates having large area for short time since the printing method is formed so as to form at one time. Further, a lot of glass substrates can be treated at one time by heating process, so that through put can be improved to enhance the mass production.

#### 4. Brief Description of the Drawings

Fig. 1 and Fig. 5 are schematic cross sectional views of the glass substrate in each process according to the manufacturing method of the present invention. Fig. 6 is a graph of the temperature condition concerning the heating or the cooling process according to the manufacturing method of the invention. Fig. 7 is a constitutional diagram of the binary alloy between silicon and tin. Fig. 8 is a schematic cross sectional view of the electric effect type thin film transistor according to the embodiment of this invention. Fig. 9 shows an equivalent circuit of the liquid crystal display.

- 1 ... glass substrate
- 2 ... silicon thin film
- 3 ... tin coated layer
- 4 ... melting layer
- 5 ... polysilicon thin film layer

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